

## Supporting Information

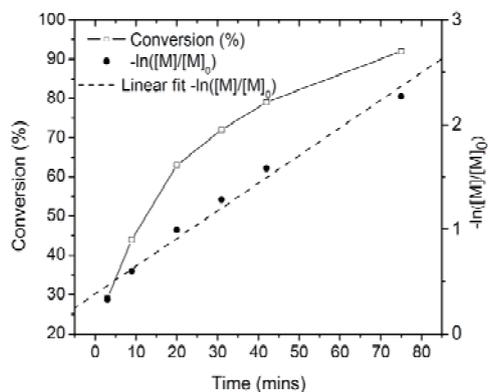
### Polynorbornenes with Pendant Perylene Diimides for Organic Electronic Applications

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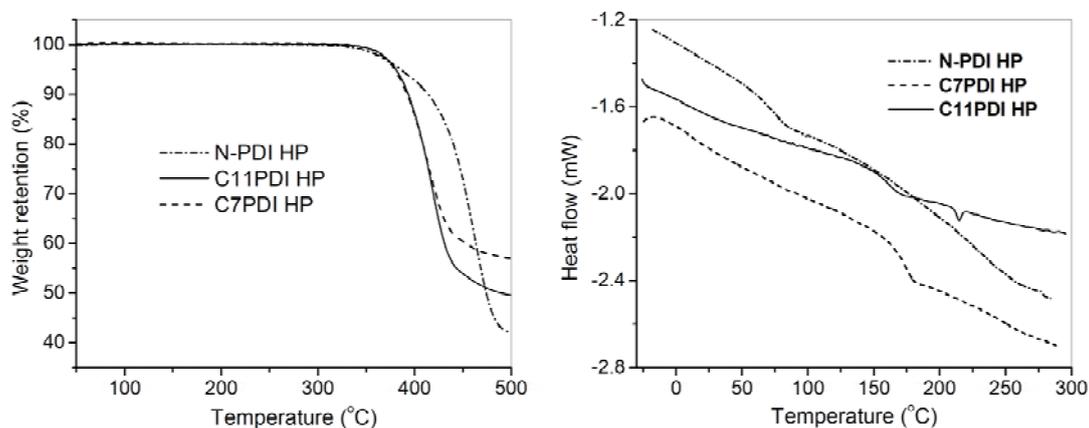
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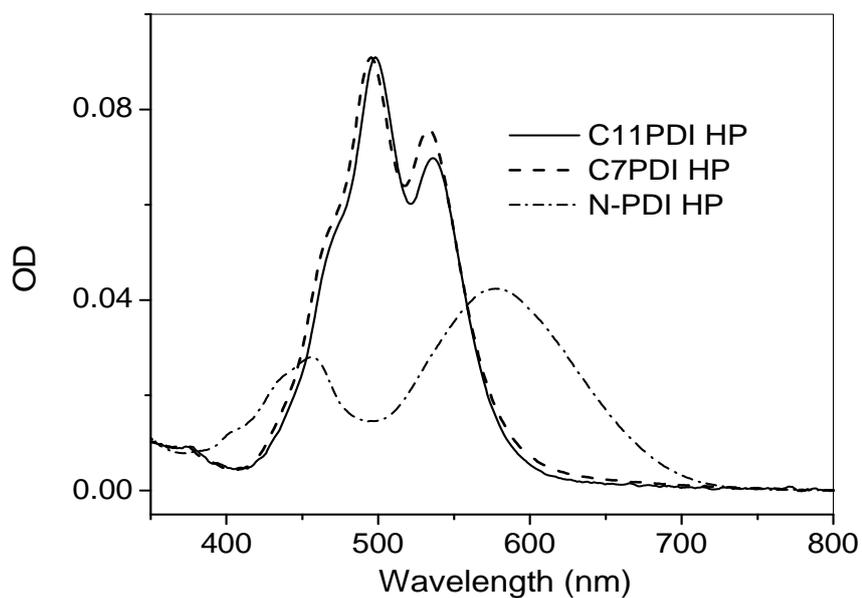
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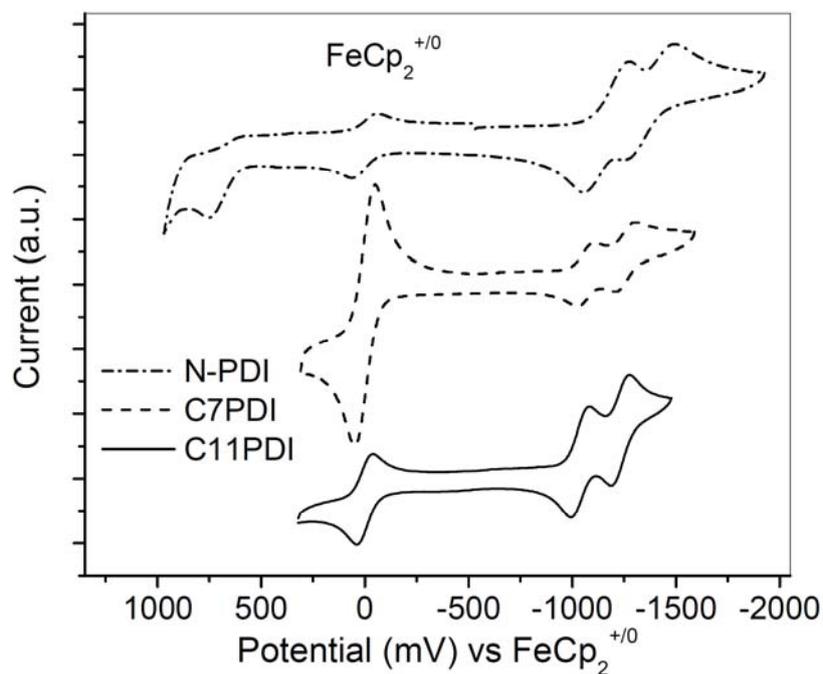
**Figure S1.** Kinetics of the polymerisation of **C11PDI (M)** in NMR tube under nitrogen initiated by the 1<sup>st</sup> generation Grubbs initiator in  $\text{CD}_2\text{Cl}_2$  as determined using  $^1\text{H}$  NMR spectroscopy. The dotted line is a fit to a first order expression in  $M$ .



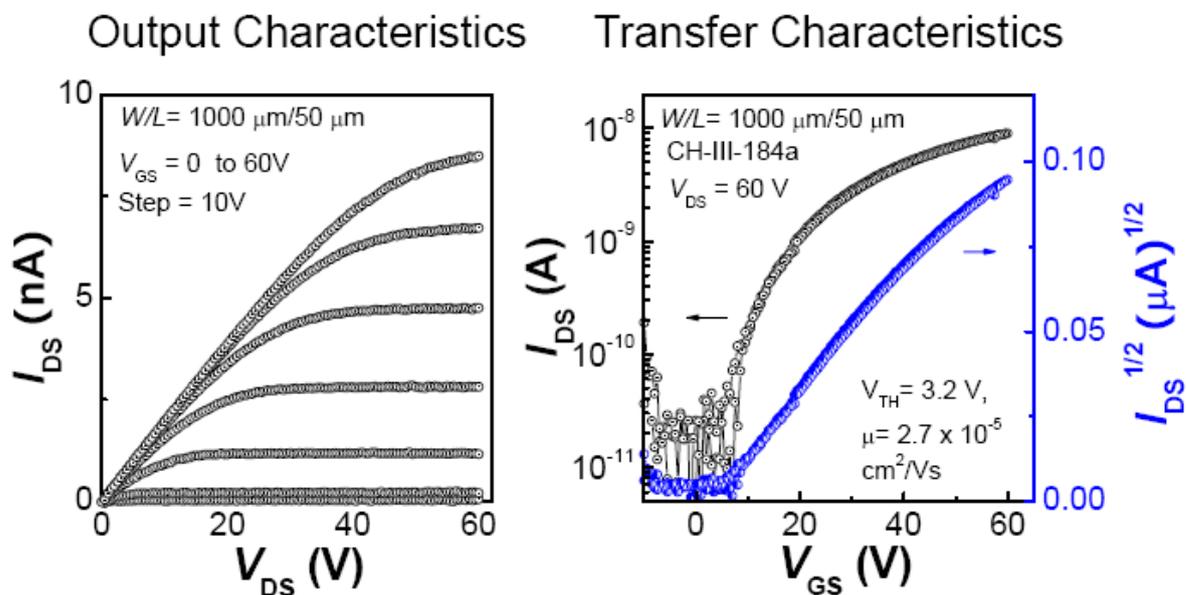
**Figure S2.** TGA traces (left) and DSC traces (second heating, right) for **N-PDI HP**, **C7PDI HP**, and **C11PDI HP**, both recorded at a heating rate of  $5\text{ }^\circ\text{C min}^{-1}$  under  $\text{N}_2$ .



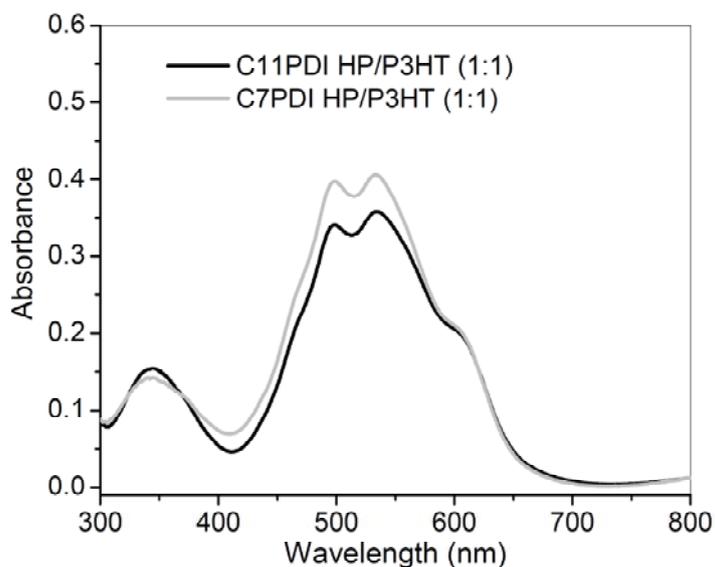
**Figure S3.** The UV-Vis absorption spectra films of PDI polymers on glass, spin-coated using  $10 \text{ mg mL}^{-1}$  solutions in toluene at 1000 rpm for 1 min.



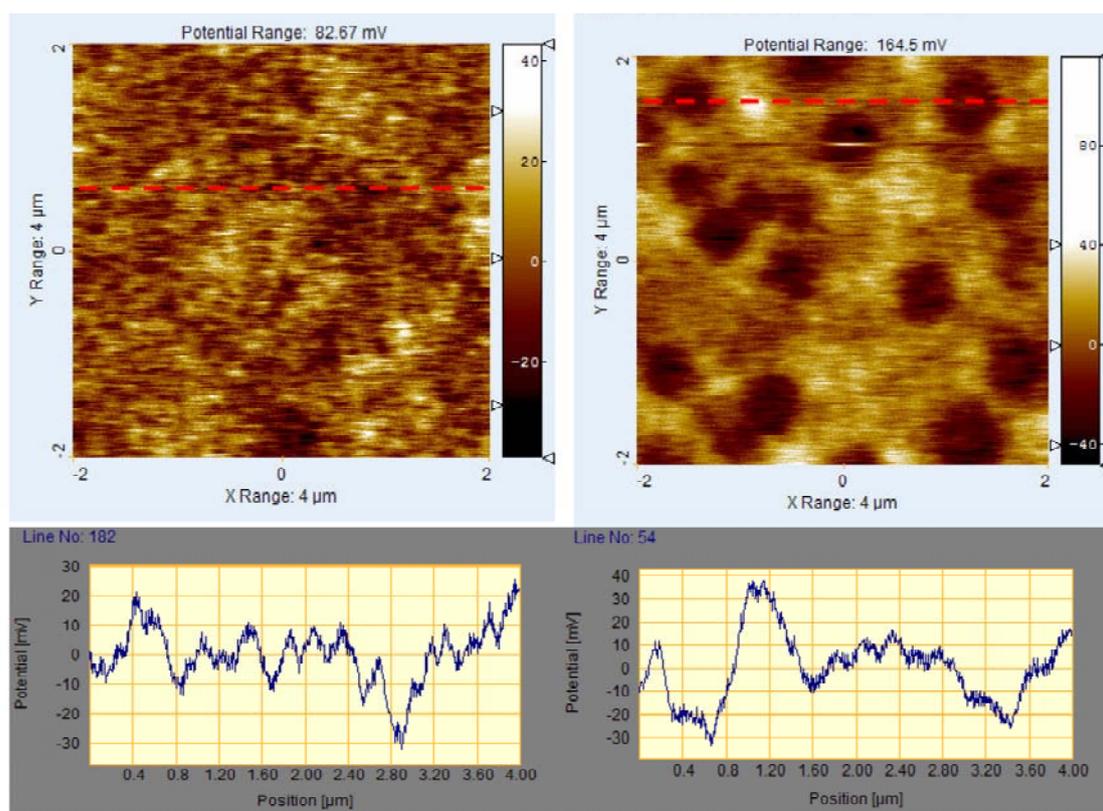
**Figure S4.** The cyclic voltammograms of **N-PDI**, **C7PDI**, and **C11PDI** in  $\text{CH}_2\text{Cl}_2 / 0.1 \text{ M } [\text{nBu}_4\text{N}][\text{PF}_6]$  recorded with a scan rate of  $50 \text{ mV s}^{-1}$ , with ferrocene as an internal reference.



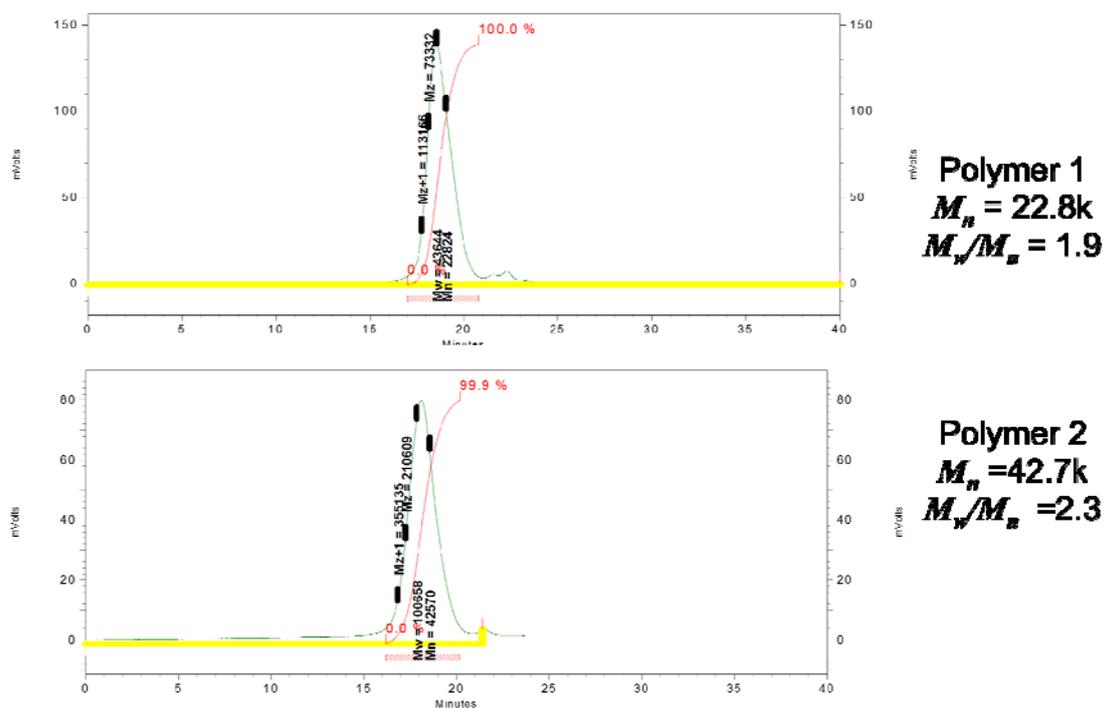
**Figure S5.** OFET device characteristics for **C11PDI HP** after annealing at 200 °C.



**Figure S6.** Absorption spectra of **C11PDI HP/P3HT** and **C7PDI HP/P3HT** films on PEDOT:PSS-coated ITO. These films were prepared in similar fashion to those used as active layers of OPV cells.



**Figure S7.** Surface potential (top two) images for P3HT:C11PDI HP (left two) and P3HT:C7PDI HP (right two) obtained by KPFM. Here, major topographical hills lead to dark areas and thus low surface potential in the images, especially for the P3HT:C7PDI HP blend. The bottom two panels represent the surface potential along the red line in the two upper images.



**Figure S8.** GPC traces of “diblock” homopolymer based on **C11PDI** after synthesis of first and second blocks.

### Additional Experimental Details

*N,N'*-Bis(1-undecyl-dodecyl)perylene-3,4,9,10-tetracarboxylic diimide.<sup>1</sup> A mixture of perylene-3,4,9,10-tetracarboxydianhydride (6.0 g, 15 mmol), 1-undecyl-dodecylamine (12 g, 35 mmol), zinc acetate (1.6 g, 8.7 mmol), and imidazole (70 g) were heated at 180 °C for 5 h before it was allowed to cool to room temperature and treated with 2 N aqueous HCl (400 mL). The mixture was then extracted with chloroform (2 × 200 mL). The organic phase was washed with water (3 × 100 mL) and dried over MgSO<sub>4</sub>. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel, using CHCl<sub>3</sub> / hexane (1:1 and then 2:1) as eluent to give the desired product as a red solid (12 g, 77%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ

8.64 (m, 8H), 5.18 (m, 2H), 2.22 (m, 4H), 1.86 (m, 4H), 1.4–1.1 (m, 72H), 0.80 (t,  $J = 6.6$  Hz, 12H). The  $^1\text{H}$  NMR spectrum is consistent with the literature.<sup>1</sup>

***N,N'*-Bis(1-heptyloctyl)perylene-3,4,9,10-tetracarboxylic diimide.**<sup>2</sup> A mixture of perylene-3,4,9,10-tetracarboxydianhydride (6.6 g, 17 mmol), 8-aminopentadecane (10 g, 43 mmol), zinc acetate (1.6 g, 8.7 mmol) and imidazole (70 g) were heated at 180 °C for 5 h before it was allowed to cool to room temperature and treated with 2 N aqueous HCl (400 mL). The mixture was then extracted with chloroform (2 × 200 mL). The organic phase was washed with water (3 × 100 mL) and dried over  $\text{MgSO}_4$ . The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography on silica gel, using  $\text{CHCl}_3$  / hexane (1:1 and then 2:1) as eluent to give the desired product as a red solid (10 g, 73%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.59–8.63 (m, 4H), 8.50–8.52 (d,  $J = 8.0$  Hz, 4H), 5.18–5.23 (m, 2H), 2.22–2.29 (m, 4H), 1.88–1.92 (m, 4H), 1.25–1.38 (m, 40H), 0.82 (t,  $J = 6.6$  Hz, 12H). The  $^1\text{H}$  NMR spectrum is consistent with the literature.<sup>2</sup>

**Compound A1.** *N,N'*-Bis(1-undecyl-dodecyl)-perylene-3,4,9,10-tetracarboxylic diimide (1.0 g, 1.0 mmol) and potassium hydroxide (powder, 0.19 g, 3.4 mmol) in *tert*-butanol (18 mL) were heated to 120 °C for 50 min under nitrogen. After the solution was cooled to *ca.* 100°C, it was treated with acetic acid (17 mL) and 2 N aqueous HCl (10 mL). The resultant mixture was stirred at room temperature overnight and then extracted with chloroform (100 mL). The organic layer was washed sequentially with water (2 × 20 mL), 0.5 N aqueous  $\text{NaHCO}_3$  (20 mL), and water (20 mL). The mixture was dried over  $\text{MgSO}_4$ , and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel, eluting with  $\text{CHCl}_3$  to give **A1** as a red solid (0.33

g, 48%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$ : 8.72–8.66 (m, 8H), 5.18 (m, 1H), 2.25 (m, 2H), 1.88 (m, 2H), 1.35–1.29 (m, 36H), 0.82 (t,  $J = 6.3$  Hz, 6H). Anal. Calcd for  $\text{C}_{47}\text{H}_{55}\text{NO}_5$ : C, 79.07; H, 7.76; N, 1.96. Found: C, 78.86; H, 7.79; N, 1.94. The  $^1\text{H}$  NMR spectrum is consistent with the literature.<sup>1</sup>

**Compound A2.**<sup>2</sup> *N,N'*-Bis(1-heptyloctyl)perylene-3,4,9,10-tetracarboxylic diimide (3.2 g, 4.0 mmol), potassium hydroxide (0.55 g, 8.4 mmol) in *tert*-butanol (90 mL) were heated to 120 °C and maintained at this temperature for 50 min under nitrogen. After the solution was cooled to *ca.* 80 °C, it was treated with acetic acid (72 mL) and 2 N aqueous HCl (50 mL). The resultant mixture was stirred at room temperature overnight and then extracted with chloroform (100 mL). The organic layer was washed sequentially with water (2 × 40 mL), 0.5 N aqueous  $\text{NaHCO}_3$  (40 mL), and water (2 × 40 mL). The mixture was dried over  $\text{MgSO}_4$  and filtered, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel eluted with  $\text{CHCl}_3$ . **A2** was obtained as a red solid (1.4 g, 59%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.69–8.50 (m, 8H), 5.18 (m, 1H), 2.24 (m, 2H), 1.86 (m, 2H), 1.34–1.20 (m, 20H), 0.81(t,  $J = 6.5$  Hz, 6H). The  $^1\text{H}$  NMR spectrum is consistent with that reported in the literature.<sup>2</sup>

***N,N'*-Bis(2-decyl-tetradecyl)-perylene-3,4:9,10-tetracarboxydimide.**<sup>3</sup> Perylene-3,4,9,10-tetracarboxydianhydride (4.0 g, 10 mmol), 2-decyl-tetradecylamine (17.0 g, 48.0 mmol) and imidazole (31 g) were combined in a round-bottomed flask with an air condenser, and the reaction flask was immersed in an oil bath at 160 °C for 3 h after which the reaction flask was removed from the oil bath. After it was cooled to room temperature, 2 N HCl aqueous (400 mL) was added. The reaction mixture was extracted with  $\text{CHCl}_3$ , dried over  $\text{MgSO}_4$ , and filtered. The solvent was removed by rotary

evaporation, and the residue was purified by column chromatography, eluting with  $\text{CHCl}_3$ , to give a red solid (10.4 g, 98%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.52 (d,  $J = 8.0$  Hz, 4H), 8.38 (d,  $J = 8.0$ , 4H), 4.09 (d,  $J = 7.5$  Hz, 4H), 1.97 (m, 2H), 1.5–1.0 (m, 80H), 0.83 (m, 12H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  163.5, 134.2, 131.2, 129.2, 126.1, 123.2, 122.8, 44.7, 36.6, 31.9, 31.7, 30.1, 29.69, 29.66, 29.65, 29.4, 26.5, 22.7, 14.1 (12 alkyl carbons missing, presumably due to overlap).<sup>3</sup>

**“Diblock”-type C11PDI HP synthesis.** C11PDI (100 mg, 0.112 mmol) was dissolved in anhydrous dichloromethane (4.0 mL) under  $\text{N}_2$  and “first generation” Grubbs initiator (1.5 mg, 0.0018 mmol) in dichloromethane (1.0 mL) was added. The reaction mixture was stirred for 5 h until all, and then part of the solution (1.3 mL) was taken out for GPC analysis (**Polymer 1**  $M_n = 22.8$  kDa,  $M_w/M_n = 1.9$  in THF, [monomer]/[initiator] = 62). To the remaining solution, C11PDI monomer (60 mg, 0.067 mmol) in anhydrous dichloromethane (1.0 mL) was added and the reaction mixture was stirred for overnight before it was added to methanol (200 mL) dropwise; the resulting red precipitate was filtered for GPC analysis. (**Polymer 2**  $M_n = 42.7$  kDa,  $M_w/M_n = 2.3$  in THF, [monomer]/[initiator] = 111).

## References

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